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G2C

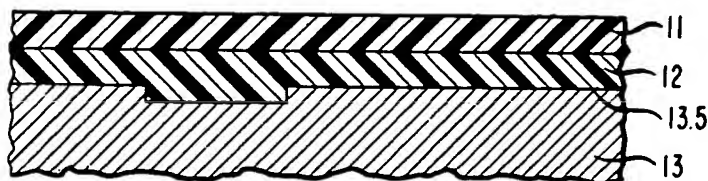
G2X

(54) Bilevel ultraviolet resist system for patterning substrates of high reflectivity

(57) A bilevel photoresist system 10 of two organic photoresists, both sensitive to deep ultraviolet (UV) radiation from the same deep UV source (e.g., Xe-Hg) and suitable for use in patterning a substrate of high reflectivity in the deep UV, comprises a top layer of a negative photoresist (e.g., the azide-phenolic resin diazodiphenyl sulfone mixed into poly (p-vinylphenol) having a thickness of about 0.5 micron, and a bottom layer of positive photoresist (e.g., polymethyl methacrylate), having a thickness about 1 or 2 microns. The top layer is thus of sufficient thickness to be substantially opaque to the deep UV radiation from the source. The top layer is patterned by projecting the deep UV light to form an image therein which is complementary to the ultimately desired pattern, followed by treating the top layer, with a suitable solvent which attacks and removes the unexposed portions thereof. Then the bottom layer is patterned by directing a collimated (parallel) beam from the deep UV source onto the bottom layer, using the thus patterned top layer as a shadow mask, followed by treating the bottom layer with a suitable solvent which attacks and removes the portions of the bottom layer thus previously exposed to the UV light. Then the thus patterned photoresist layers can be used as a protective mask for etching the top surface of the substrate in accordance with the desired pattern.

FIG. 1

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1/2

FIG. 1

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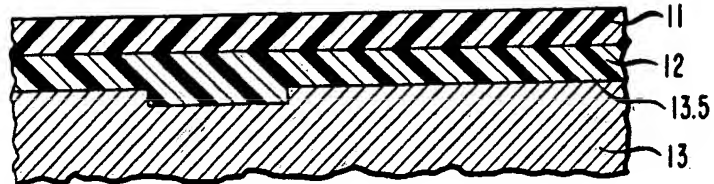


FIG. 2

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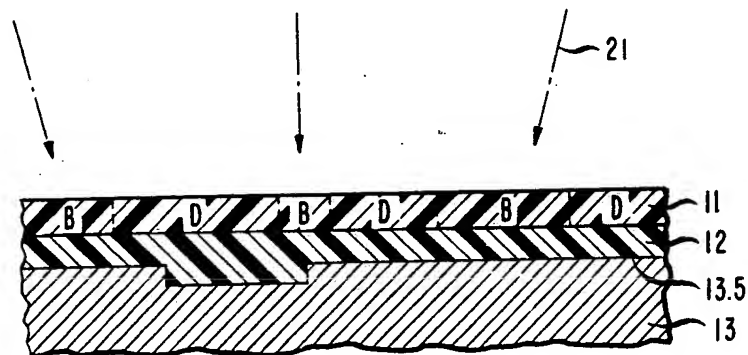


FIG. 3

10

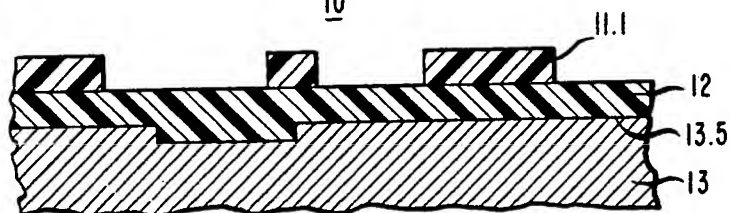


FIG. 4

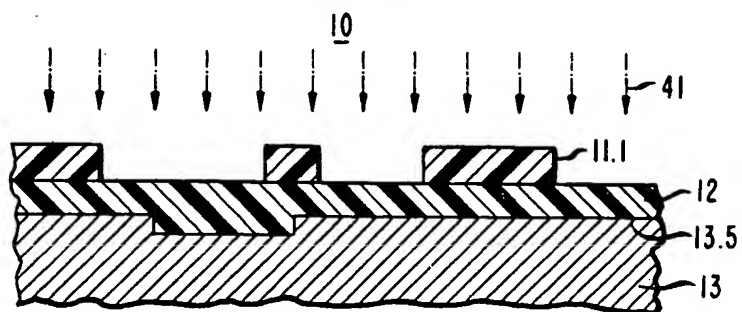


FIG. 5

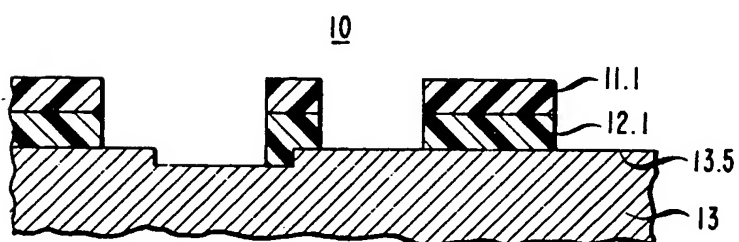
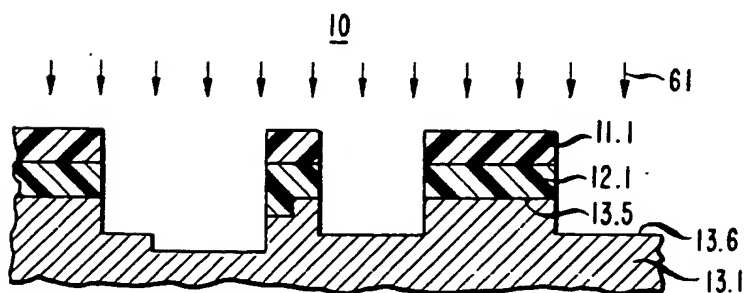


FIG. 6



SPECIFICATION

Bilevel ultraviolet resist system for patterning substrates of high reflectivity

5 This invention relates to a method for making semiconductor devices comprising the steps of coating a substrate to be processed with a lower layer of photoresist, coating the lower layer with an upper layer of photoresist, using optical apparatus to project a focused image of first ultraviolet light on the upper layer, the substrate being reflective of the first ultraviolet light, developing the upper layer to form a first mask, exposing the masked lower layer to second ultraviolet light, developing the lower layer to form a second mask, and thereafter processing the substrate.

10 In the manufacturing of devices such as semiconductor integrated circuits, patterning (by geometrically selectively etching) a top surface layer of a substrate in accordance with a desired configuration is typically accomplished using a patterned protective layer comprising a patterned photoresist (photo-sensitive etch resistant material), which is located in contact with the top surface of the substrate. The photoresist layer is patterned in accordance with the desired configuration of patterning of the top surface of the substrate, and the thus patterned photoresist layer serves as a geometrically selective protective mask against etching the top surface of the substrate. The photoresist layer itself is typically patterned by first geometrically selectively illuminating it with a pattern of optical (or photo) radiation. The pattern is arranged to produce in the photoresist layer a pattern of bright and dark regions in accordance with the ultimately desired substrate surface pattern (or its complement, as explained more fully below). Then the photoresist is developed by treating it with a solvent, which develops the resist by selectively dissolving it in accordance with the pattern of radiation.

A photoresist can be either a "positive" photoresist (dissolves where previously illuminated by photoradiation) or a "negative" photoresist (dissolves where not previously illuminated). In any event, it should be of sufficient thickness to avoid pinhole problems (typically a thickness of at least 0.4 micron or more). Accordingly, the layer of photoresist after development is patterned in accordance with the pattern (positive photoresist) or complementary pattern (negative photoresist) of the radiation. Using the thus patterned layer of photoresist as a protective mask against etching, the top surface layer of the substrate is patterned by selective removal of portions thereof in accordance with the pattern of the photoresist by means of a treatment with an etchant which attacks the material of the top surface layer of the substrate but not the material of the photoresist. In this way, the top surface layer of the substrate is patterned in the desired configuration, the pattern (or complement thereof) of the optical radiation having been imparted to the photoresist, and thence the resulting pattern of the photoresist having been imparted to the top surface layer of the substrate.

Optical radiation used thus to define the pattern in a photoresist is typically in the near ultraviolet (wavelength range between about 3000 and 4000 Angstroms) or deep ultraviolet (wavelength between about 2000 and 3000 Angstroms), in order to achieve submicron pattern definition (feature size). In any event, optical diffraction effects limit the feature size to approximately one wavelength or more, depending upon the nature and geometry of the optical system used for defining the pattern.

As known in the art, there are problems associated with imparting the desired pattern to the photoresist from the optical radiation, depending upon the details of the method used therefor. There are three typical such methods: optical contact printing, optical proximity printing, and optical projection printing. The first two have limitations that will not be discussed herein.

In the technique of optical projection printing, an optical projection system, typically comprising lenses and/or mirrors, is used to focus the resulting projected optical beam of radiation as an image in the photoresist. This image has a pattern of bright and dark regions, as determined by the projection system, in accordance with the ultimately desired pattern to be imparted to the surface of the substrate. A major problem here, encountered in case the top surface of the substrate is not planar, is a blurring of the image, and hence an undesirable blurring or spreading of the ultimate photoresist pattern, caused by a nonvanishing depth of optical image focus which is less than the height of steps (nonplanarity) of the top surface of the substrate. This problem can be mitigated by using a bilevel photoresist system, that is, two layers of photoresists of different materials, one layer on top of and in contact with the other. Both layers advantageously have flat (planar) top major surfaces. In order for the bottom photoresist layer to have a flat top major surface (to be contacted by the top layer), the bottom layer has a sufficiently large thickness to enable formation of the flat (planar) top surface. In order to avoid problems caused by nonvanishing depth of focus, the top layer of photoresist has a sufficiently small (and uniform) thickness, typically about 0.5 micron (i.e., less than the depth of image focus). For submicron feature definition or resolution (less than one micron) of the pattern, both photoresist layers are sensitive to ultraviolet (UV) radiation.

For example, U. S. Patent No. 4,211,834 issued to Lapadula et al on July 8, 1980, entitled "Method of Using O-Quinone Diazide Sensitized Phenol-Formaldehyde Resist as a Deep Ultraviolet Light Exposure Mask," teaches a bilevel photoresist system of organic materials composed of: (1) a bottom layer of positive photoresist which is sensitive to deep ultraviolet optical radiation but which is both not sensitive and not opaque to near ultraviolet (near UV) radiation (λ between about 3000 and 4000 Angstroms), such as a layer of PMMA (polymethyl methacrylate), and (2) a top layer of photoresist which is opaque to deep ultraviolet optical radiation (λ between about 2000 and 3000 Angstroms) but which is sensitive but not opaque to near UV, such as a phenol-formaldehyde photoresist. This bilevel

system is formed upon the top surface of a substrate to be patterned. The system is first exposed to a first optical beam in the form of a projected optical beam focused to an image pattern of bright and dark regions in the top layer. The beam, and hence the resulting bright regions of the image, has significant amounts of radiant energy in the near ultraviolet range. The top layer is developed with a solvent that attacks and dissolves portions of the top layer in accordance with the focused image pattern--that is, portions corresponding to bright regions of the image are removed, portions corresponding to dark regions remain intact. Then a second beam in the form of a collimated (parallel) beam of unpatterned optical radiation is directed at the bottom layer through the top (now patterned) layer. The beam of collimated radiation then everywhere floods the top surface of the intact portion of the top layer and of the then exposed portions of the bottom layer, but significant amounts of this radiation cannot reach those portions of the bottom layer located underneath intact portions of the top layer, because the top layer is opaque to deep UV. This collimated beam contains significant amounts of deep UV radiation at wavelengths below 2600 Angstroms to which the bottom photoresist layer, but not the top photoresist layer, is sensitive. Accordingly, development by a solvent that selectively dissolves only the exposed portions of the bottom photoresist layer results in a patterning of the bottom layer in accordance with the previous patterning of the top photoresist layer and hence in accordance with the image pattern of the first projected optical beam. Then the top surface layer of the substrate underlying the bottom photoresist layer can be patterned by an etching process using the bottom (and top) layer(s) of the thus patterned photoresist system as a protective mask against the etching.

A major problem with the foregoing bilevel system stems from reflection of the projected near UV radiation by the top surface of the substrate. Such reflection produces a standing wave optical pattern, particularly in the top photoresist layer, which produces in the top photoresist layer an undesirable standing wave pattern of bright regions or spots in the top layer which are located at areas where it should be dark for proper pattern definition. The problem arises, for example, in systems where the top surface layer of the substrate is aluminum, which is highly reflecting in the ultraviolet. This problem can be mitigated by using for the top layer--instead of an organic material--an inorganic negative photoresist layer such as germanium-selenium as described, for example, by K. L. Tai, et al, "Submicron Optical Lithography Using an Inorganic Resist/Polymer Bilevel Scheme," *Journal of Vacuum Scientific Technology*, Vol. 17, pp. 1169-1176, (1980). However, such an inorganic layer requires an expensive vacuum deposition step instead of a relatively inexpensive process of spinning-on photoresists which are made of organic materials. Therefore, it would be desirable to have a completely organic bilevel ultraviolet photoresist system which avoids the standing wave problem caused by substrate reflectivity.

In any such photoresist system, it is also important that each layer should be selected so as not to cause interface problems with the neighboring underlying layer, that is, problems at an interface of the two layers where there is a blending of the photoresist materials of the two layers which would hinder proper development of the underlying layer.

These problems are solved in accordance with the invention in a bilevel ultraviolet resist system characterized in that the first ultraviolet light has a wavelength in the deep ultraviolet range, the upper layer is an organic material, is sufficiently thin to be within the depth of focus of the optical apparatus at the deep ultraviolet wavelength, is sensitive to deep ultraviolet light, and has a sufficient thickness to be opaque to the deep ultraviolet light.

In the drawing:

Figure 1 is a view in cross section of a bilevel deep ultraviolet photoresist system for patterning a substrate in accordance with a specific embodiment of the invention;

Figures 2 through 6 illustrate in cross section the bilevel system of Figure 1 during various successive steps of patterning a substrate in accordance with a specific embodiment of the invention.

A bilevel organic photoresist system located upon a top surface of an optically reflecting substrate comprises a top organic negative photoresist layer which is sensitive to deep ultraviolet (UV) radiation, and is at the same time substantially opaque to both deep and near UV radiation, together with a bottom organic positive photoresist layer which is sensitive to either deep or near (or both) UV radiation. Advantageously, both the top and bottom photoresist layers are made of materials which are sensitive to a given deep ultraviolet wavelength, or to a given group or band of wavelengths, so that the same UV source can be used for patterning both the top and the bottom photoresist layers. By "substantially opaque" is meant that the thickness of the (top) photoresist layer is sufficient to reduce the intensity of the deep ultraviolet radiation after propagating through the layer to less than about 10% of its initial (incident) value; that is, the UV intensity at the bottommost portions of top photoresist layer is not enough to produce any significant sensitizing and hence any significant effect on the patterning of the bottom layer by subsequent development (in solvent, for example). Thus, in particular, after propagating through the bottom photoresist layer and reflection by the top surface of the reflecting substrate, the amount of deep UV which is available for producing undesirable standing waves in the top photoresist layer is too small to cause any significant undesirable effect on the patterning of the top photoresist layer. On the other hand, the thickness of the negative photoresist layer is advantageously sufficiently small so as to be within the depth of focus of deep UV radiation, typically a thickness in the approximate range of 0.4 to 0.8 micron. An organic photoresist material that has been found to be thus suitable for the top photoresist layer is an azide-phenolic resin: specifically, diazidodiphenyl sulfone, a photosensitive azide compound, mixed with the phenolic resin poly(p-vinylphenol), sold as

"Raycast RD2000N" by Hitachi Chemical Company America, Ltd. and described in greater detail as "MRS-1" in a paper entitled "Azide-Phenolic Resin Photoresists for Deep UV Lithography" by T.

- 5 Iwayanagi et al, published in *IEEE Transactions on Electron Devices*, Vol. ED-28, No. 11, (Nov. 1981), pp. 1306-1310. A thickness of about 0.5 to 0.6 micron of this azide compound is useful and is substantially opaque to deep UV. The bottom photoresist layer
10 can be PMMA (polymethyl methacrylate), for example, or other positive photoresist of organic material sensitive to deep UV radiation advantageously which can be produced by the same UV source as that which can be used for sensitizing the top
15 photoresist layer. In this case the deep UV source used for patterning the top layer should not also contain substantial amounts of near UV radiation to which both the top layer is not opaque and the bottom photoresist layer is photosensitive. Approp-
20 priate optical filters can be used for thus suppressing such near UV radiation.

This invention's use of a negative photoresist for the top layer of a bilevel photoresist system alleviates the above-mentioned interface problem en-
25 countered when both layers are positive photoresists (positive upon positive photoresist systems). This problem does not arise in a negative upon positive photoresist system because the solvent used for patterning the top (negative) layer is
30 designed to remove only the nonilluminated portions of the negative photoresist; i.e., no photochemical change in the top layer occurs or is needed at portions thereof where removal thereof by the solvent is desired. In the positive upon positive
35 photoresist system, however, the solvent for the top layer is designed to remove only the portions of the top photoresist material which have been illuminated and have thereby undergone photochemical change; and hence at the interface of the top and
40 bottom photoresists, where there is a blending of top and bottom photoresist materials, there are photochemical reaction products (of blended material) which can be sufficiently different (from the unblended material) as to inhibit proper dissolving
45 of the top photoresist material at the interface, whereby subsequent development of the bottom layer is undesirably inhibited.

Referring now to the drawing, Figure 1 shows a bilevel photoresist system 10 for deep ultraviolet
50 photolithography comprising a top negative photoresist layer 11 of organic material located upon a bottom positive photoresist layer 12 of another organic material located upon a top surface 13.5 of a substrate 13 to be patterned by deep ultraviolet
55 photolithography. The substrate 13 is essentially aluminum, which is reflective of the deep UV radiation to be used. The aluminum substrate 13 is typically formed as the top layer of an underlying silicon integrated circuit (not shown). Other reflec-
60 tive metals or metal-like materials may be used instead of aluminum, such as gold, platinum, or metal silicide.

The negative photoresist layer is essentially an azide-phenolic resin which is photosensitive to all
65 wavelengths in a second set of deep UV

wavelengths. A deep UV optical beam is projected through a patterned opaque mask and directed onto the top surface of the negative photoresist layer where the beam is focused as an optical image in
70 this negative layer. This image has a pattern of bright and dark regions which corresponds to the complement of the desired pattern of areas to be removed from the top surface of the substrate (the bright regions of the image overlying areas of the
75 substrate not to be removed, the dark regions overlying areas to be removed). The beam (unavoidably) contains radiation of at least one wavelength λ_1 of the second set to which the positive photoresist is also sensitive (i.e., λ_1 is also in the first set). The
80 negative photoresist advantageously is made sufficiently thick to be opaque to any such wavelength as λ_1 , in order to prevent UV light of such wavelength(s) from entering the positive photoresist layer in regions thereof where it would undesirably sensitize
85 this positive layer. The beam also (unavoidably) contains at least one other wavelength λ_2 of the second set to which the positive photoresist layer 12 is not photosensitive but not opaque and of which the substrate is reflective; and therefore the negative
90 photoresist layer advantageously is made sufficiently thick to be opaque to any such wavelength as λ_2 , in order to suppress the standing wave problem. Furthermore, the negative photoresist layer advantageously is made sufficiently thin so that it is within
95 the depth of focus of all the wavelengths of the second set that are contained in the beam, in order to avoid blurring of the image in this photoresist layer.

The bottom photoresist layer 12 is a positive
100 photoresist sensitive to the deep UV, such as PMMA having a (minimum) thickness of about one micron. This layer is typically formed on the top surface 13.5 of the substrate 13 by spin coating with PMMA (9% in chlorobenzene) using a spin speed of about 5000
105 rpm. After baking at about 150° C for about 60 minutes, a photosensitive azide (diluted in the ratio of about 7 parts azide compound to: 3 parts cyclohexanone) is spun onto the top surface of the PMMA using a spin speed of about 6000 rpm, to
110 yield a thickness for the negative photoresist layer 11 of about 0.5 micron. Although a thickness of about 0.3 micron would be sufficient for the layer 11 to be opaque with respect to the deep UV radiation, a thickness of about 0.5 micron is preferred, in order to
115 avoid pinhole problems. However, this thickness can also be anywhere in the approximate range of 0.4 to 0.8 micron. The resulting bilevel system 10 is then baked at about 70° C for about 30 minutes.

As shown in Figure 2, a deep UV projected light
120 beam 21 is formed and directed through an opaque patterned mask (not shown) onto the bilevel system 10 by a standard optical projection system (not shown). The beam 21 is thereby focused to an image pattern of bright and dark regions (labeled B and D in
125 Figure 2) in the negative photoresist layer 11 in accordance with the pattern of the mask. The deep UV beam is supplied by a standard deep UV lamp source (not shown). The optics are such as to transmit deep UV of wavelengths in the range of
130 about 0.200 to 0.240 micron, for example, or alterna-

tively 0.240 to 0.280 micron. The UV source is typically a 500 watt xenon-mercury lamp. The UV radiation is typically about 100 millijoule/cm² or about 140 millijoule/cm², respectively for the

5 abovementioned wavelength ranges. Next, as indicated in Figure 3, development of the top layer 11 converts it into a patterned top layer 11.1, that is, patterned in accordance with the image of the mask 31. Specifically, the previously bright regions B

10 remain and the previously dark regions D (Figure 2) are removed by the development step. For example, this development can be accomplished by treatment with a solution of 1:4/MF312:H₂O where MF312 is composed of hydroxides of ammonium ions.

15 Then, after another baking (about 150° C for about 60 minutes), the bilevel system 10 is subjected to another UV exposure. Specifically, as indicated in Figure 4, a collimated (parallel) beam 41 of deep UV radiation is directed uniformly all over (floods) the

20 top surface of the system. The beam 41 delivers a radiation dose of about 3000 millijoule/cm², for a range of wavelengths between about 0.200 and 0.240 micron. The same deep UV source can thus be used for providing the beam 41 as for previously

25 providing the beam 21 (Figure 2). After development by treatment with a suitable solvent, such as methyl isobutyl ketone, for about 60 seconds, the bottom photoresist layer 12 becomes a patterned bottom photoresist layer 12.1 as indicated in figure 5.

30 Finally, the system 10 is subjected to a standard chlorine plasma 61, (Figure 6), in order anisotropically to remove (etch) the then exposed portions of the aluminum substrate 13. During this etching, the remaining patterned photoresist layer 11.1 and/or

35 12.1 inhibit any etching of the top surface 13.5 of the substrate 13 in regions thereof underlying the remaining portion of these photoresist layers. The resulting top surface 13.6 of the resulting patterned aluminum substrate 13.1 is thus at a lower horizontal

40 level than the original top surface 13.5. Ordinarily the chlorine plasma etching is continued until the entire thickness of the aluminum is removed. The photoresist layers 11.1 and 12.1 can then be removed, as by a treatment with O₂ (oxygen) plasma.

45 Although the invention has been described in detail in terms of a specific embodiment, various modifications can be made without departing from the scope of the invention. For example, instead of PMMA, other positive organic photoresists can be

50 used for the bottom photoresist layer such as poly(methyl methacrylate-co-3-oximino-2-butanone methacrylate) or "P(MOM)", poly(methyl methacrylate-co-3-oximino-2-butanone methacrylate-co-methacrylo nitrile) or "P(M-OM-CN)", poly(methyl

55 isopropenyl ketone) or "PMIPK", or poly(methyl methacrylate-co-indenone) or "PMI"—all of which are photosensitive to deep UV in the wavelength range of about 0.240 to 0.280 micron. Finally, instead of a xenon-mercury light source for the deep UV

60 radiation, a mercury light source or a deep UV laser can be used.

CLAIMS

65 1. A method for making semiconductor devices

comprising the steps of coating a substrate to be processed with a lower layer of photoresist, coating the lower layer with an upper layer of photoresist, using optical apparatus to project a focused image of

70 first ultraviolet light on the upper layer, the substrate being reflective of the first ultraviolet light, developing the upper layer to form a first mask, exposing the masked lower layer to second ultraviolet light, developing the lower layer to form a second mask,

75 and thereafter processing the substrate, wherein the first ultraviolet light has a wavelength in the deep ultraviolet range, the upper layer is an organic material, is sufficiently thin to be within the depth of focus of the optical apparatus at the deep ultraviolet

80 wavelength, is sensitive to deep ultraviolet light, and has a sufficient thickness to be opaque to the deep ultraviolet light.

2. The method according to claim 1, wherein the upper layer is essentially an azide-phenolic resin.

85 3. The method according to claim 1 or 2, wherein the second ultraviolet light is of the same wavelength as the first ultraviolet light.

4. The method according to claim 1, 2, or 3, wherein the upper layer is a negative photoresist

90 and the lower layer is a positive photoresist.

5. The method according to claim 4, wherein the upper layer has a thickness of 0.4-0.8 micron.

6. The method according to claim 5, wherein the first and second ultraviolet light is supplied by a

95 single xenon-mercury lamp.

7. The method according to claim 1, wherein the upper layer is essentially an azide-phenolic resin of diazidodiphenyl sulfone mixed with poly(p-vinylphenol) having a thickness of 0.4-0.8 micron.

100 8. A method of making semiconductor devices, substantially as hereinbefore described with reference to the accompanying drawings.

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